PREPERATION OF HYDROXYAPATIE-ALUMINA COATED ZIRCONIA COMPOSITES

A THESIS SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Ceramic Engineering

By
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Department of Ceramic Engineering
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CERTIFICATE

This is to certify that the thesis entitled, "PREPERATION OF HYDROXYAPATIE-ALUMINA COATED ZIRCONIA COMPOSITES" submitted by Shri **PAULJIN KOCHUPYLOTH** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

Date:30.05.07

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Date: 30.05.07 PAULJIN KOCHUPYLOTH

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ABSTRACT

Hydroxyapatite (HAp) bioceramics as bone substitute materials have unique biocompatibility feature among phosphate groups. How ever, the low fracture strength and poor fatigue resistance due to the instability of OH^- groups limit the use of HAp for load-bearing applications. In present research, we investigated the effects of TZP powder coated with Al_2O_3 on the phase stability of HAp .The coated TZP powder was expected to be effective as a reinforcing agent for the HAp. In order to prepare the composite, calcined ZrO_2 powder was dispersed in aqueous aluminium chloride solution (0.75mol/liter). The suspension was added drop by drop into ammonia solution which is kept at a pH around 6-7.This pH is carefully selected by considering zeta potential of boehmite and Zirconia for promoting heterofloculation. The resultant precipitate was calcined at 850^0C/4hour. The calcined powder was added to required amount of diammonium hydrogen orthophosphate and calcium nitrate (Ca/P ratio 1.67). This combined suspension was added drop by drop into ammonia solution kept at a pH around 10. The precipitates were dried, calcined at 850^0C, followed by compaction of the calcined powder and sintering at 1250^0C. The results show that the degree of decomposition of HAp is least in case of HAp-TZP composite where as the reaction tendency of HAp with Al_2O_3 is prominent. This adverse reaction increases with the increase in alumina content in the system. Thus the obtained result contradicts the previously found observations, i.e. the tendency of reaction of HAp with ZrO_2 is more feasible than that with Al_2O_3. For further comparison we studied different HAp- Al_2O_3 coated ZrO_2. It was inferred that the reaction tendency of HAp- Al_2O_3 coated ZrO_2 composites with HAp is less with respect to HAp- Al_2O_3. The reaction tendency is found to increase in accordance with increase in Al_2O_3 content in the composites.

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1.1 .Background and Objective

Calcium phosphate group is the largest and the most important inorganic part of hard tissues constituting bones and dentine material in vertebrate animals. Synthetic calcium phosphate has been shown to be quite similar, crystallographically and chemically, to the natural materials in the bone and has several medical applications including replacement of bony and periodontal defects, alveolar ridge, maintenance of spine fusion, and ear/eye implantation. Hydroxyapatite (HAp) bioceramics as bone substitute materials have many advantages such as biocompatibility . Apatite [$Ca_{10}(PO_4)_6X_2$] materials have unique biocompatibility feature among phosphate groups; X in the formula represents hydroxyl(OH^-) group for hydroxyapatite (HAp), fluoride (F^-) group for fluorapatite, chloride (Cl^-) group for chloroapatite. In particular, porous HAp implants have served as bone substitute in the clinics for long time. Porosity is required for two purposes: (a) weight reduction and (b) the ability to rapidly deliver calcium to support histological processes [1]. HAp with controlled porosity is analogous to the natural ceramic in the bone and is bioactive in the sense that it is a non-toxic compound and interfacial bonds are able to develop between HAp and the living tissues leading to enhanced mechanical strength of the overall structure. The porosity aids in tissue growth and their binding with the HAp. However, lower mechanical strength of pure HAp has hampered its use as a bone implant material because of conflicting requirements of porosity and strength. In addition, HAp also has the potential to be used in dental applications. Both mechanical strength and bioactivity of HAp depend strongly upon its microstructure such as grain size and grain size distribution, porosity and its shape and distribution, and material crystallinity [2] . This leaves much freedom in the hands of materials designers to improve and tailor the properties of this material depending upon the application. As a result, HAp powders have been synthesized using several methods including wet-chemical method in aqueous solutions, sol–gel method, hydrothermal method, thermal deposition, conversion of coastal corals, and continuous precipitation.

However, the low fracture strength and poor fatigue resistance due to the instability of OH^- groups limit the use of HAp for load-bearing applications. Besides the HA-coating technique, efforts have also been made to improve the

mechanical properties of HAp-based ceramics in order to utilize the bone- bonding ability of the material. Composites made of HAp and other ceramic powders, metal particles or polymers have been studied. Such composites have not yet been applied clinically, partly because of the technical difficulties [3].

The potential of ceramics as biomaterials relies up on their compatibility with the physiological environment. Bioceramics are compatible because they are composed of ions commonly found in physiological environment and of ions showing limited toxicity to body tissue.

Inert bioceramics undergo little or no chemical change during long-term exposure to the physiological environment. Even in those cases where these bioceramics may undergo some long term chemical or mechanical degradation, the concentration of degradation product in adjacent tissue is easily controlled by the body's natural regulatory mechanisms [4]. Tissue response to immobilized inert bioceramics involves the formation of very thin, several micrometers or less, fibrous membrane surrounding the implant material. Inert bioceramics may be attached to the physiological system through mechanical interlocking, by tissue in growth into undulating surfaces. The nearly inert ceramics most used in surgical implants is alumina and Zirconia[5].

Among the ceramic reinforcements, alumina (Al_2O_3) has been used in orthopaedic applications due to its excellent wear resistance. However, when this oxide is used as a reinforcing agent for HAp, the decomposition of HAp to β- TCP occurs severely, resulting in poor densification and reduced mechanical properties . Therefore, efforts must be made to produce fully densified HAp – Al_2O_3 composites without the decomposition [5].

1.2. Structure of Hydroxyapatite and its crystallographic properties

The term apatite describes the family of compounds having similar structures but not necessarily having identical composition. Hence apatite is a description and not a composition. Calcium hydroxyapatite is a compound of a definite composition $Ca_{10}(PO_4)_6(OH)_2$, and a definite crystallographic structure . The structure of calcium-hydroxyaptite with exact atomic position is shown by Beevers and MCintyre form a mineral and later refined by Kay *et al* with a synthetic HAp[1]. Calcium hydroxyapatite belongs to the hexagonal system with a space group p63/m. This space group is

characterized by a six fold c-axis perpendicular to three equivalent a-axes (a1, a2, a3) at angles 120^0 to each other. The ten calcium atoms belong to either Ca_1 or Ca_2 subsets depending up on their environment. Four calcium atoms occupy the Ca_1 positions, two at levels z=0 and other two at z=0.5. Rest six calcium atoms occupy the Ca_2 positions; one group of three calcium atoms describing a triangle located at z=0.25, the other group of three at z=.75 surrounding the OH^- groups at the corners of unit cell at z=.25 and =.75 respectively. The six phosphate $(PO_4)^{3-}$ are in helical arrangement from levels z=.25 to z=.75. The network of $(PO_4)^{3-}$ groups provide the skeletal framework which gives the apatite structure its stability [1].

The apatite structure is very hospitable and this substitution results in change in properties. Elliott and Young showed that Cl substitution causes the loss of hexagonal symmetry and exhibit monoclinic symmetry, because of the alternating position of the Cl and enlargement of the cell in the b direction. For example substitution of F causes a contraction in the a-axis without changing the c-axis, is usually associated with an increase in the crystallinity, reflecting increase in the crystal size (or decrease in the crystal strain) and imparts greater stability to the structure. F substituted apatites are less soluble than F-free synthetic and biological apatites[3].

Carbonates, CO_3^- can substitute either for hydroxyl or the phosphate groups designated as type A or type B substitution respectively. These two types of substitution have opposite effects on the lattice parameters. [5]. The type A of larger planar CO_3^- group for smaller linear OH^- group cause an expansion in the a-axis and contraction in the c-axis dimensions , while type B of smaller planar CO_3^- group for a larger tetrahedral PO_4^{3-} group cause a contraction in the a-axis and the expansion in the c-axis dimensions compared to the CO_3^- free aptites. LeGeros and co-workers also demonstrated that the coupled CO_3^- for PO_4^{3-} and Na^+ for Ca^{2+} substitution cause changes in the apatite crystal from acicular to rods to equi-axed crystals with increase in the carbon content and in dissolution properties; the CO_3^- substituted aptite being more soluble than CO_3^- free synthetic apatites. Sr for Ca or Mg for CA substitution causes an increase in the extent of dissolution of the apatite. Magnesium and carbonate have synergistic effects on the crystallinity and dissolution properties of synthetic apatites. Magnesium and fluoride or

carbonate and fluoride have antagonistic effects, the fluoride effect being the more dominant one.

Biological apatites differ from pure HA in stoichiometry, compostion, and crystallinity and in other physical and mechanical properties. Biological apatites are usually calcium deficient and are always carbonate substituted. The carbonate is usually substituted for the phosphate groups in a coupled manner referred to as type B substitution. The coupled substitution is necessary for balance the charges[6].

❖ *Composition of synthetic dense hydroxyapatite (HAp)*

Pure HAp has the theoretical composition of Ca-39.68 (mol%), P-18.45 (mol%) with Ca/P molar ratio-1.667 and lattice parameters a - 9.442A^0, c - 6.881 A^0. If Ca/P is lower than 1.67 β-TCP and other phases such as tetracalcium phosphate will be present with HAp phase in the sintered material depending up on the temperature and condition of sintering. If Ca/P is higher than 1.67 CaO will be present with the HA phase [1].

1.3. Alumina ceramic as implant material

High density, high purity (>99.5%) alumina is used in load bearing hip prosthetics and dental implants because of its combination of excellent corrosion resistance, good biocompatibility, high wear resistance, high strength[7].

1.4. Zirconia ceramic as implant material

Zirconia is exceptionally inert in the physiological environment and Zirconia ceramics have an advantage over alumina ceramics of higher toughness and higher flexural strength and lower Young's modulus [8]. However there are three major controversies regarding Zirconia. One is the reported strength reduction with time in physiological fluids.The second is its wear properties and third is the potential radioactivity of the material. The deleterious martenstic transformation from tetragonal to monoclinic phase in yittria doped zirconia due to aging is well documented. Alumina and Zirconia ceramics have similar roughness and wetting characteristics. The only major difference in their surface in their surface properties is that alumina is much harder. The wear rate of Zirconia –Zirconia coupling was 5000 times that of alumina-alumina coupling. Zirconia is often accompanied by radioactivity elements with a very long half –life, such as

thorium and uranium. These elements are difficult and expensive to separate from zirconia [8].

1.5. What makes a material a composite?

Composite materials are formed by combining two or more materials that have quite different properties. The different materials work together to give the composite unique properties, but within the composite one can easily tell the different materials apart – they do not dissolve or blend into each other.

Hydroxyapatite materials have high bioactivity, but their inherent low fracture strength and toughness render them unable to use for practical purposes. Alumina is added to improve in mechanical properties without diminution of biocompatibility.

1.6. Why HAp- alumina coated Zirconia composite?

There are to major approaches for the improvement in mechanical properties of the HAp. One is to fabricate a macrocomposite material .Metal implants coated with HAp, which are widely used these days, belong to this class of material. However large differences in physical and thermal properties between the metals and the Hap create limitations to this approach. [6]Another approach is to make a microscale composite material .HAp reinforced with other ceramics in the form of the powder, platelets, or fibers belong to this type of material. This approach has attracted much attention since the successful development of ceramic matrix composite materials.

To be effective as a reinforcing agent for a ceramic-matrix composite material, the following conditions should be satisfied .First the strength and the elastic modulus of the second phase must be higher than those of the matrix. Secondly, the interfacial strength between the matrix and the second phase should be neither too weak nor too strong [8]. For an appropriate interfacial strength, no excessive reaction should between the matrix and the second phase. In addition the coefficient of thermal expansion of the second phase should not differ too much from that of the matrix. Otherwise, subsequent to densification, micro cracks will form around the second phase during cooling and seriously detoriate mechanical properties of the composite material. In the

case of biomaterials, the biocompatibility of the reinforcing agent is another important factor that should be considered [8].

A reinforcing material for the HAp satisfying all of these requirements has not yet been found. Most material reacts with HAp to form metal oxides and tricalcium phosphate leading to serious reduction in the biocompatibility of HAp. Partially stabilized Zirconia has been commonly used as reinforcement for many ceramics because of its high strength and fracture toughness [8]. Bio inertness is another merit of zirconia. However extensive reaction between the HAp and the ZrO_2 to form TCP and fully stabilized zirconia is a big disadvantage of this approach.

Alumina classified as a bioinert material, has been widely investigated as a reinforcing agent for HAp .When large alumina platelets were added, the fracture toughness of the HAp increased with out the excessive reaction between the HAp and the Al_2O_3 however improvement in strength was minimal because of the formation of micro cracks around the platelets due to the large difference in CTE between Al_2O_3 and HAp . on the other hand ,when fine Al_2O_3 powder was used ,formation of micro cracks was circumvented; however , the improvement in mechanical properties was limited due to relatively low mechanical properties of Al_2O_3 itself. Therefore, it is desirable to combine the advantage of both materials as reinforcements for the HAp; the excellent mechanical properties of the ZrO_2 and the chemical inertness of Al_2O_3 with respective t the HAp .Tetragonal zirconia polycrystal (TZP) powder coated with Al_2O_3 in one possible approach [7].

In present research, we investigated the effects of TZP powder coated with Al_2O_3 with Al_2O_3 on the mechanical properties of HAp .The coated TZP powder was expected to be effective as a reinforcing agent for the HAp .Although Al_2O_3 also reacts with HAp to form TCP, the degree of the reaction is much less compared to that of ZrO_2 .Furthermore, the presence of small amounts of TCP is not necessarily harmful for HAp as a bio material because of its bio-resorbability [9].

Chapter 2

LITERATURE REVIEW

Kong et al [6] studied the effect of reinforcement of Hydroxyapatite by ZrO_2 coated with Al_2O_3. The coated powder was prepared by coating TZP with boehmite. The boehmite (AlOOH) solution was prepared by hydrolyzing an aluminium isopropoxide solution. The boehmite was dispersed in distilled water at a concentration of 0.1g/L. Surface charges of the ZrO_2 and the AlOOH were measured as a function of solution pH with a zeta meter. Various amount of coated powder were mixed with the HAp by ball milling I distilled water for 24 h with Al_2O_3 balls as a media to break the HAp agglomerates. The powder mixture were hot pressed in a graphite mould at 1200 ^{0}C in flowing Ar atmosphere with an applied pressure of 20MPa.The strength and the fracture toughness of hot pressed HAp were improved significantly by the addition of tetragonal zirconia polycrystal powder coated with Al_2O_3. The coating was effective in reducing the deleterious reaction between HAp and ZrO_2 .When 15vol% ZrO_2 and 30 vol% Al_2O_3 powders were added to the HAp by coating method, the strength and the fracture toughness of the specimens were 300MPa and 3MPa.m$^{1/2}$ respectively, which are about three times higher than ot the pure HAp. The preservation of ZrO_2 particles as a tetragonal phase in the HAp matrix was attributed to the improvement in the mechanical properties.

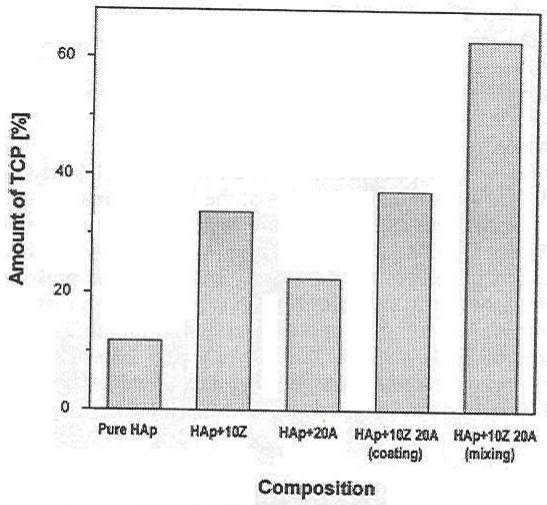

Fig 2.1- Amount of β-TCP formed in different composites [6]

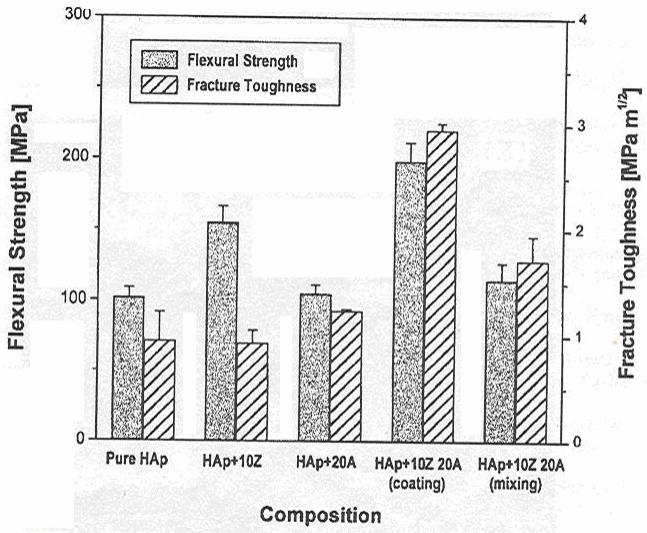

Fig 2.2- Flexural strength and fracture toughness of HAp composites [6]

Young-Min Kong et al [7] conducted the study for improvement in biocompatibility of ZrO_2–Al_2O_3 nano-composite by addition of HAp. It was reported that biocompatibility of zirconia–alumina (ZA) nano-composites in load-bearing applications such as dental/orthopedic implants was significantly enhanced by the addition of bioactive HAp. The ZA matrix was composed of nano-composite powder obtained from the Pechini process and had higher flexural strength than conventionally mixed zirconia–alumina composite. The Pechini process is based on the formation of a network which is composed of a polymeric precursor and a cationic network modifier. In the Pechini process, the metallic ions are distributed homogeneously on an atomic scale throughout the polymeric network. Such a structure eliminates the need for long-range diffusion during the subsequent formation of metal oxides. Therefore, in conventional Pechini processes, the precursor forms a homogeneous single phase oxide of precise stoichiometry at a relatively low temperature. In this experiment, we used Zr and Al as the metallic ions in the Pechini process to make a nano-composite powder. Since zirconium and aluminum are unlikely to form a compound, the intimacy between the Zr and Al ions captured in a polymeric network enables them to form a nano-sized

composite powder. Metal chlorides ($ZrCl_2O \cdot 8H_2O$, $AlCl_3 \cdot 6H_2O$, $YCl_3 \cdot 6H_2O$) were used as the cationic sources; citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, CAM) and ethylene glycol ($C_2H_6O_2$, EG) were used as the polymeric matrix. A stoichiometric mixture of Zr and Y source solution (3 mol% Y_2O_3 doping in ZrO_2) and Al source solution were used as the starting materials. The compositional ratio of ZrO_2 to Al_2O_3 was 4:1 by weight, because this composition showed the highest flexural strength. After mixing the metallic source solutions with CAM-EG solution, the resultant mixture was heated to 130°C to promote esterification between CAM and EG. Finally, the gel was dried, crushed and calcined at 800°C. The obtained powders were ball-milled in ethanol for 48 h with ZrO_2 balls to reduce the secondary particle size.

The total polymer content in the powder precursor was as high as 90 wt%. When 90% of polymer was added to the solution, the particles began to coalesce so as to form a nano-composite powder composed of ZA. All of the particles were composed of 100–200 nm clusters, which contained zirconia nano-crystallites whose size was about 10 nm, as shown in. Since a greater number of nucleation sites were formed in the gel as the polymer content increased, the zirconia gradually grew into nano-sized particles and eventually became a nano-composite powder through their merging with alumina.

The starting powders were commercial HA (Alfa Aesar Co., Ward Hill, MA, USA) and the above-mentioned ZA nano-composite powder. In addition, commercially available ZrO_2 (3Y-TZP, Tosoh Co., Tokyo, Japan) and Al_2O_3 (AKP50, Sumitomo Co., Osaka, Japan) were used for the purpose of comparison. The ZA nano-composite powders (composition of 80 wt% ZrO_2–20 wt% Al_2O_3) were mixed with HA (specific compositions of up to 40 vol%) by ball milling for 24 h. After the mixed slurry was dried, crushed and sieved, the resulting powders were hot-pressed in a graphite mold at 1400°C with an applied pressure of 30 MPa for 1 h. The phase of the hot-pressed bodies was analyzed with an X-ray diffractometer (M18XHF, MAC Science, Yokohama, Japan), and the density of the specimens was measured by the Archimedes method. The fractured and polished surfaces were observed with a SEM (JSM-6330F, JEOL, and Tokyo, Japan). The flexural strength was measured by means of the four-point flexure test with a cross-head speed of 0.5 mm/min, and inner- and outer-spans of 20 and 40 mm,

respectively (number of SAMPLES=7) . The tensile surface of the specimens was polished using diamond slurries (1 μm finish).

Strong zirconia–alumina (ZA) nano-composites were fabricated with the addition of bioactive HA for the purpose of improving their biocompatibility. Hot pressing the nano-composite powder at 1400^{o}C resulted in the formation of BCP of HA/TCP within the composites. The resultant body has high mechanical strength, while maintaining the excellent biocompatibility. As the amount of HA was increased, the proliferation and differentiation behaviors of the osteoblast-like cells on the composites increased.

Khalil et al [8] observed the structural and electrical properties of zirconia/hydroxyapatite porous composites. The porous zirconia/ hydroxyapatite composites containing 7.58–32.89% ZrO_2 were sintered at 1000 and 1250 °C. It was reported that relative porosity (ΔP) decreased with increased ZrO_2 content at both the firing temperatures. Sintering at 1250 °C, however, was accompanied by higher ΔP as a consequence of a partial transformation of HA (hydroxyapatite) to β-TCP (β-tricalcium phosphate) besides partial stabilization of the ZrO_2 tetragonal phase. The higher ZrO_2 content and/or sintering temperature resulted in reduced a-axis of HA and increased its c-axis. On the other there was also, a reduction of both a- and c-axes in the formed β-TCP denoting cell contraction with higher ZrO_2 content and sintering at 1250 °C. Scanning electron microscopy (SEM) showed the presence of HA and ZrO_2 in the composite sintered at 1000 °C. The transformation of monoclinic ZrO_2 to the tetragonal phase and HA to β-TCP at 1250 °C was assured. The dielectric constant ε' and loss ε'' values were minimum at low measuring temperatures (298–593 K) and low frequencies (frequency range 10^2–1×10^6 HZ). Multiple relaxation peaks and frequency shifts in conductivity/ frequency relations were related to zirconia content, elimination of CO_3^{2-} and porosity as well as multiple phases achieved at high sintering temperature.

Juliano Pierri et al [9] prepared and characterized Alumina/zirconia composite coated by biomimetic method. A bioactive zirconia -toughened alumina (ZTA) composite was developed for orthopedic applications. This composite was obtained by slip casting of suspension powder mixtures.

Biomimetic processes were used to grow a bone-like apatite layer on composite substrates using sodium silicate solution as a nucleating agent and simulated body fluids. The composites, with or without coating, were characterized by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS), and their apparent density was determined by the Archimedes method. The composites obtained by this process possessed the expected stiffness and dimensions and their density values were similar to those of the composite's theoretical density (98.8%TD). The morphology of the hydroxyapatite formed on the composite surface was homogeneous and composed of small globules, characterizing a carbonated hydroxyapatite. The results of the tests indicated that the method employed to produce the composite and its coating was efficient under the conditions of this study.

Chin-Yi Chiu et al [10] observed the effect of zirconia addition on the microstructural evolution of porous HAp. They studied the mechanical properties of HAp –alumina coated zirconia ceramics. Improvement of the mechanical properties of HAp has thus far attracted wide attention of the researchers. Among the many approaches that has been employed to improve the mechanical properties, the reinforcement of HAp by zirconia addition is a major one. The expected increase of the strength and toughness of Hap-ZrO_2 will be significant, provided there will be no reaction between HAp and ZrO_2. For example, the strength and toughness of a 50%HAp/50%ZrO_2 composite can reach 439 MPa and 2.5 MPa $m^{0.5}$, respectively [ ]. However, the HAp and ZrO_2 readily react with each other above 1000 °C. Below the temperature, the densification is usually not possible unless very special processes such as hot-isostatic pressing (HIP), spark plasma sintering (SPS) are employed. However, considerable cost is usually involved of applying these special processes.

The product of the reaction between HAp and ZrO_2 is calcium zirconate ($CaZrO_3$), which is bio-inert to human tissue. The penalty of such a reaction is the consumption of the Ca from HAp. As the amount of ZrO_2 is large, HAp would be consumed completely after sintering, and α- or β-tricalcium phosphate ($Ca_3(PO_4)_2$) formed. Previous studies were mostly concentrating on the reaction between HAp and ZrO_2. However, the effect

of such a reaction on the microstructure evolution of HAp during sintering has attracted relatively little attention. In the present study, a small amount, <5 vol%, of ZrO_2, is added into HAp. The effect of the ZrO_2 addition on the microstructure evolution during sintering is investigated. The mechanical properties of the porous HAp-$CaZrO_3$ composites are also measured.

The HAp powder used in the present study was prepared by using a solid-state reaction process with $Ca(OH)_2$ and $CaHPO_4$ as the starting materials. The amount of $Ca(OH)_2$ and $CaHPO_4$ was controlled such that a Ca/P ratio of 1.67 was achieved. These two powders were mixed together by ball milling in alcohol for 4 h. The grinding media used were 10 mm Ø zirconia balls. The slurry of the powder mixtures was dried with a rotary evaporator. The calcination of the powder mixture was carried out at 1200 °C for 2 h. The calcined powder mixtures were crushed and sieved. The particle size of the HAp powder was determined with a laser particle size analyzer (Master 2000, Malvern Co,USA). The HAp powder was then mixed with 1, 3 or 5 vol% of zirconia powder (ZrO_2 + 3 mol.% Y_2O_3, TZ-3Y, d_{50} = 230 nm, Tosoh Co., Japan) through ball milling. After drying and sieving, rectangular bars with the dimensions of 6 mm × 6 mm × 46 mm were formed by pressing uniaxially at 60 MPa. Sintering was performed at 1300 °C for 2 h in air.

It has been proven that of zirconia reduces not only the sintering shrinkage, but also decreases the size of HAp grains. Both the strength and toughness of porous HAp were decreased slightly due to the formation of $CaZrO_3$ phase.

Chapter 3

MATERIALS AND METHODS

3.1. Preparation of Al_2O_3 powder

3.2. Preparation of HAp-Al_2O_3 composite powder

3.3. Preparation of 3 Y_2O_3 - TZP powder using Y_2O_3 and $ZrOCl_2$

3.4. Preparation of HAp- ZrO_2 composite powder

3.5. Preparation of Al_2O_3 coated ZrO_2 powder

3.6. Preparation of HAp and Al_2O_3 coated ZrO_2 composite powder

3.7. Characterization

3.1. Preparation of Al_2O_3 powder

Aqueous aluminium chloride solution (0.75mol/litre) was taken. Then the solution was added drop by drop into ammonia solution kept at a pH around 6. The whole solution was added to ammonia solution and the precipitates were stirred for 30 minutes. The precipitates were allowed to settle over night followed by decantation and washing. The resultant precipitates were dried followed by calcination at 850^0C/4hour. The calcined powder was ground properly with the help of a mortar.

3.2. Preparation of HAp-Al_2O_3 composite powder

Required amount of diammonium hydrogen-orthophosphate and calcium nitrate were taken keeping the ca/p ratio 1.67. Both powders were made into 0.6 mol/liter solutions. The solutions were mixed with constant stirring. Initially, a turbid solution formed and it was made into a clear solution by addition of conc.HNO_3 .Then calcined Al_2O_3 powder was dispersed in solution. The resultant solution was kept in ultrasonic bath for 3 minutes for ensuring proper dispersion of Al_2O_3 powder and to avoid formation of agglomerates. The mixture was added drop by drop into ammonia solution which was kept at a pH around 10. After adding whole solution into ammonia solution the mixture was kept under stirring for 2 hours. Then the solution was allowed to settle over night. The decantation and washing were carried out. The resultant precipitate was dried in a dryer for 24 hours. The dried powder was calcined at 850^0C/4hour. The calcined powder was ground properly with a help of a mortar. The fine powder was mixed with PVA and pellets were made by pressing. The pellets were sintered at 1250^0C.

3.3. Preparation of 3Y - TZP powder using Y_2O_3 and $ZrOCl_2$

The required amount of $ZrOCl_2$ was taken and made into a solution. 3mol% Y_2O_3 was taken and digested in HNO_3 .The Y_2O_3 solution was poured into $ZrOCl_2$ solution. The precipitate was poured into a beaker which was maintained at pH>9 with constant stirring. Then procedure mentioned in 3.1 was followed.

3.4. Preparation of HAp- ZrO_2 composite powder

Required amount of diammonium hydrogen-orthophosphate and calcium nitrate was taken keeping the ca/p ratio 1.67. The 0.6 mol/liter solutions of each powder was prepared. Both solutions were mixed with constant stirring .At first a turbid solution was formed and it was made into a clear solution by addition of conc.HNO_3 .Then calcined ZrO_2 powder was dispersed in the suspension. The resultant suspension was kept in ultrasonic bath for 3 minutes for ensuring proper dispersion of ZrO_2 powder inorder to avoid formation of agglomerates. Then the mixture was added drop by drop into ammonia solution which was kept at a pH around 10. The precipitate was kept under stirring for 2 hours. Then the precipitate was allowed to settle over night. Then decantation and washing is carried out. Then procedure mentioned in 3.2 was carried out.

3.5. Preparation of Al_2O_3 coated ZrO_2 powder

Calcined ZrO_2 powder was dispersed in aluminium chloride solution (0.75 mol/litre) in water. The resultant suspension was kept in ultrasonic bath for 3 minutes for ensuring proper dispersion of ZrO2 powder. Besides that ultrasonic bath avoided the formation of agglomerates. Then the mixture was added drop by drop into ammonia solution (pH around 6). This pH was carefully selected by considering zeta potential of boehmite and Zirconia in order to ensure heterocoagulation. The fig 3.1 shows the zeta potential variation of Boehmite and Zirconia[6]. The precipitate was kept under stirring for 30 minutes. Then procedure mentioned in 3.1 was followed

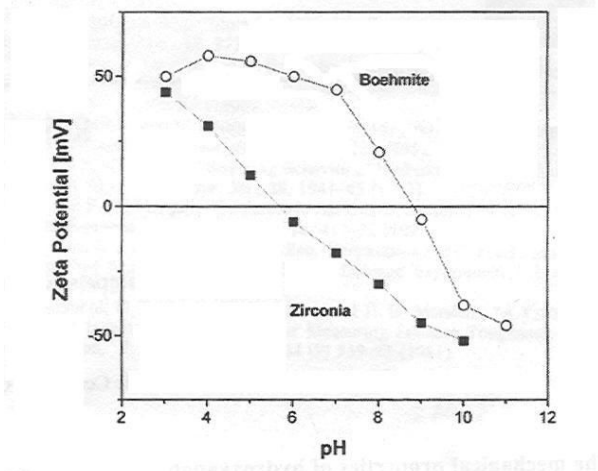

Fig-3.1. Zetapotential variation of Boehimite and Zirconia [6]

3.6. Preparation of HAp and Al_2O_3 coated ZrO_2 composite powder

Diammonium hydrogen-orthophosphate and calcium nitrate was taken keeping the ca/p=1.67. The starting concentration of both the materials was 0.6 mol/liter. Solutions were mixed under constant stirring .At first; some turbidity was observed which was removed by adding conc.HNO_3. Then calcined Al_2O_3 coated ZrO_2 powder was dispersed in solution. The resultant solution was kept in ultrasonic bath for 3 minutes. Then the suspension was added drop by drop into ammonia solution which was kept around pH 10 which resulted in the precipitation of amorphous Hap and Al_2O_3 coated ZrO_2. Then procedure mentioned in 3.2 was carried out.

Synthesis of HaP-Al_2O_3 coatedZrO_2Composites

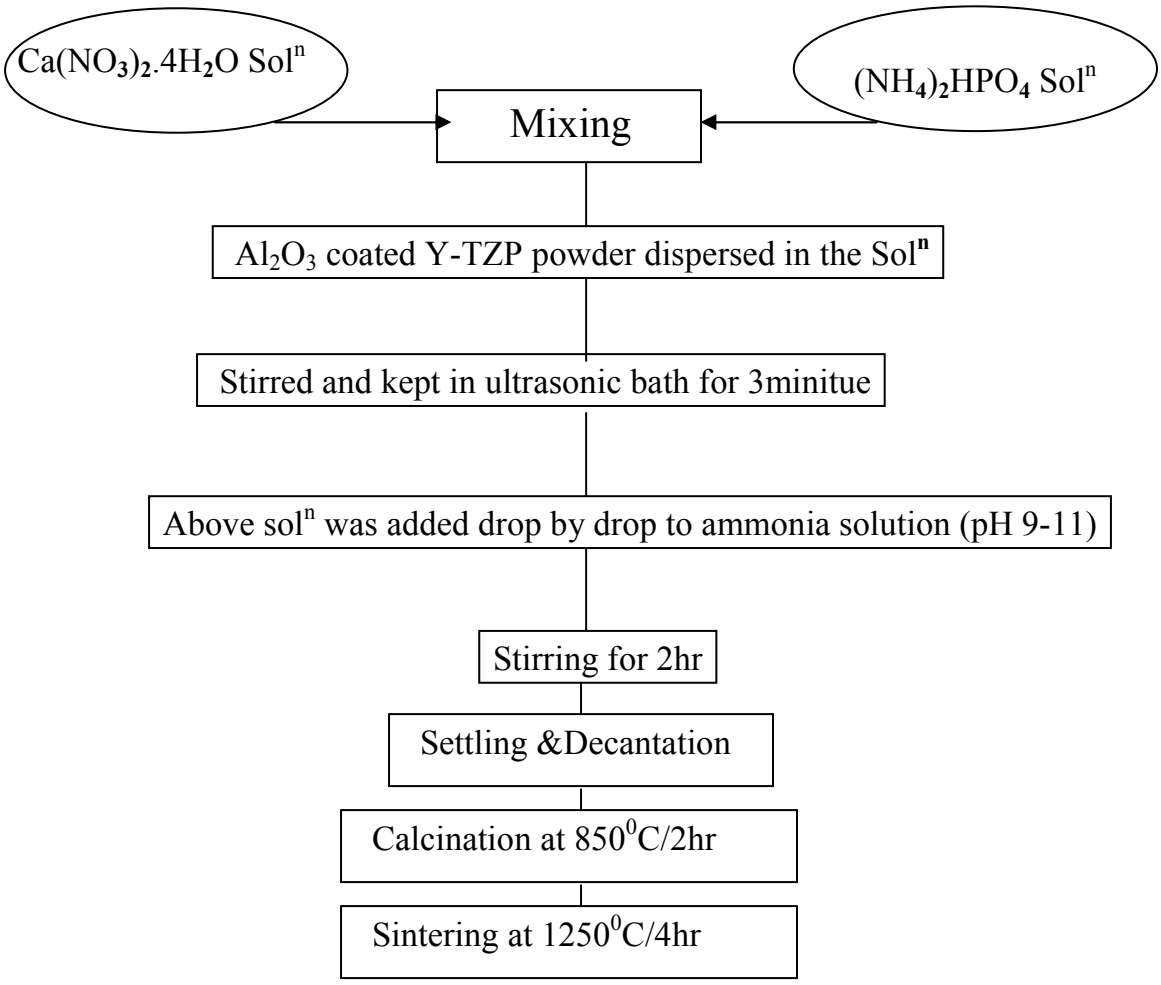

Fig.3.2- Synthesis of HaP-Al_2O_3 coatedZrO_2Composites

3.7. Characterization

- Measurement of density

The densities of sintered pellets were measured using Archimedes principle. Kerosene (ρ=.81) was used as the liquid displacing medium. The working formula was

$$\text{Density of pellet } (\rho) = \frac{\text{Dry. Wt x 0.81}}{\text{(Soaked .Wt – Suspended .Wt)}}$$

- Phase analysis by XRD

The composition of the sintered composites was determined by X-ray diffraction (XRD: Phillips Analytical, Holland). X-rays were produced by a monochromatic source (Cu Kα, λ = 1.54 A^0, 40 kV, 55 mA) and, all the XRD patterns were recorded in the same conditions (scan range: 2θ = 20^0-80^0; time per step: 0.4s; scan step: 0.080; type of scan: continuous).

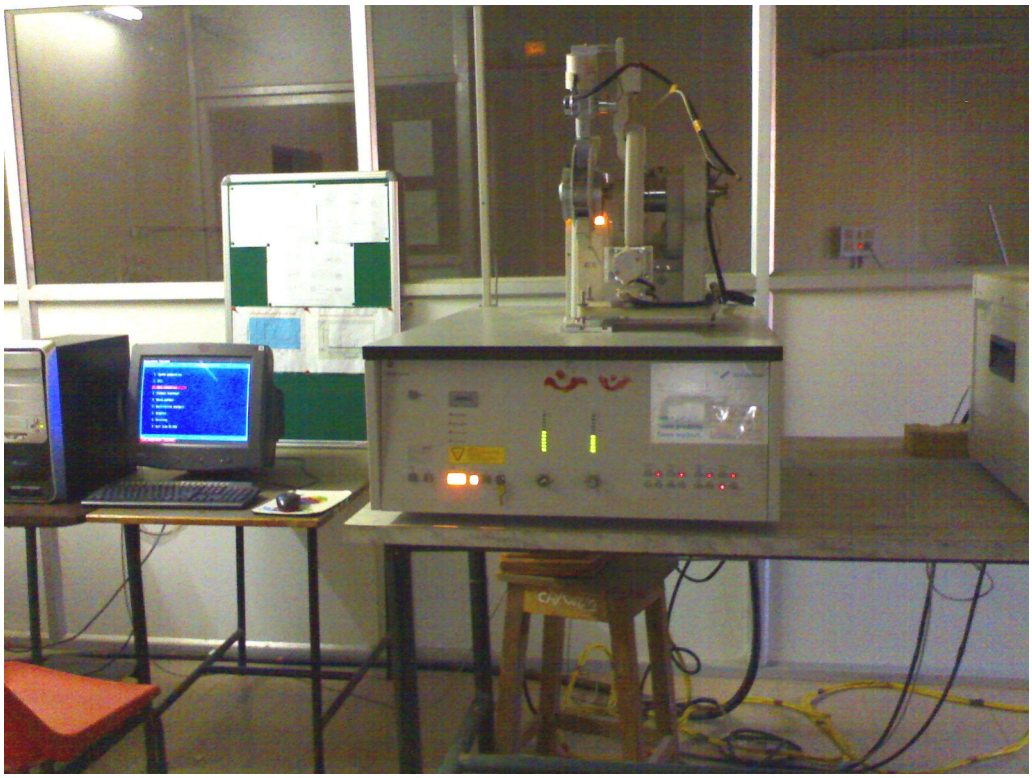

Fig 3.3.XRD machine (Philips Analytical, Holland)

Chapter 4

RESULTS & DISCUSSION

The calcined samples of calcined HAp- Al_2O_3 coated ZrO_2 composites were bearing HAp and TZP as the major phases. The schematics were shown in Fig.4.1. The deleterious phase such as β=TCP, Calcium zirconate, and Calcium aluminate were not found in the calcined pellets. They were so termed as deleterious due to their adverse effect on the density of sample and consequent effect up on the mechanical properties of final composite. The mere presence of these phases causes decomposition followed by the removal of H_2O at high temperature. These reactions hampered the sinterabilty of matrix material and as a result mechanical properties were diminished.

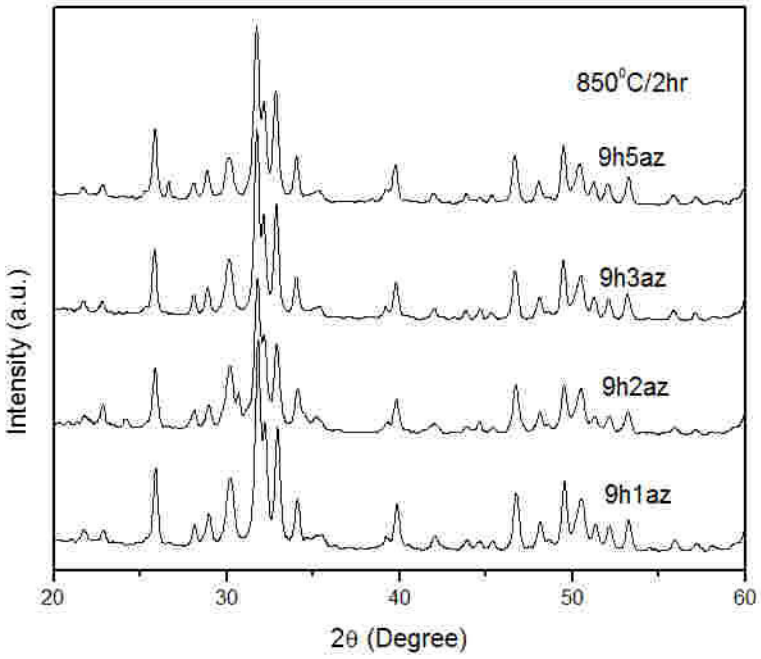

Fig.4.1 The combined XRD plot of various calcined HAp- Al_2O_3 coated ZrO_2 composites.

In order to observe the effect of sintering on the samples, XRD patterns at 1250^0C/4hr of the respective samples were taken. The details were depicted in Fig 4.2 .

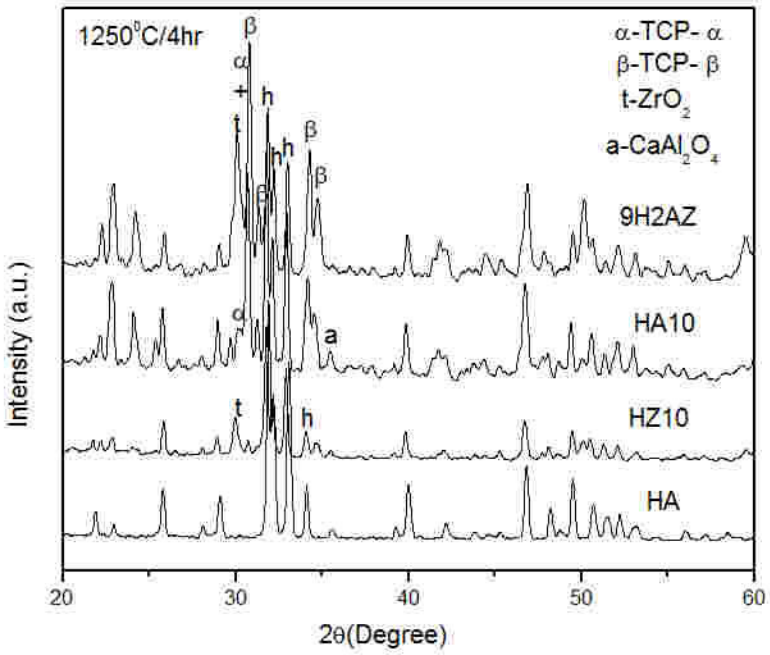

Fig 4.2. The combined XRD plots of Sintered samples.

Fig 4.2 shows that HAp contains three major peaks at d–values 2.819 A^0 ($2\theta = 31.47^0$), 2.71 A^0 ($2\theta = 32.9^O$), 2.52 A^0 ($2\theta = 34.2^0$). These d values match with the standard d-values of stochiometic HAp. This confirms that prepared HAp was stochiometric on nature. The measured density of the HAp was 98%.

The HAp-TZP composite had 91.2 % density. It contains HAp(62%), TZP(22.68%) as major phases. The composite also contains minor amounts of β–TCP (16%) after sintering.

HAp- Al_2O_3 composite contains significant amount of β–TCP (44%) after sintering at 1250^0C/4hr. Consequently, the HAp content was reduced to 49%. The composite also possess minor amounts of calcium aluminate (16%). The effect of prominent amounts of β–TCP was reflected in composite density (62.32%).

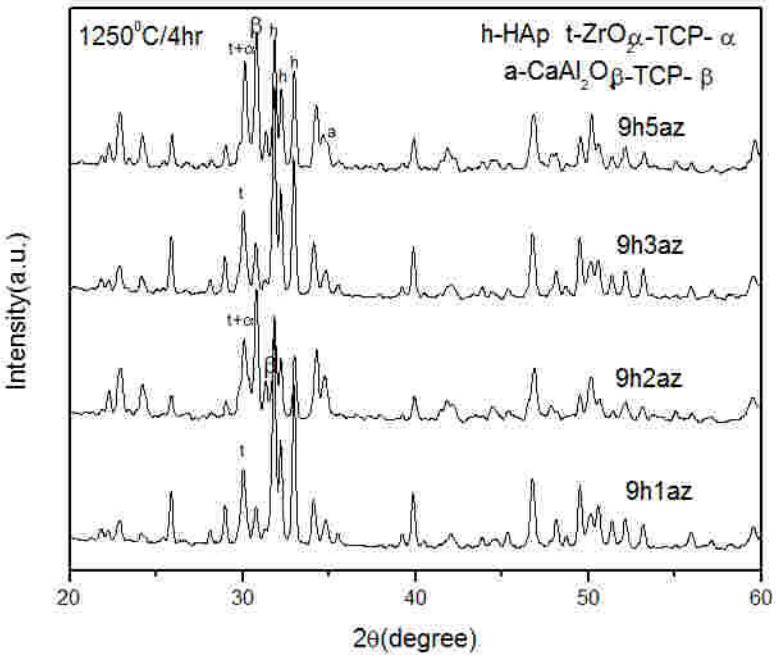

Fig 4.3 -The diffraction pattern of sintered HAp- Al_2O_3 coated ZrO_2 composites

Fig 4.3 shows the diffraction pattern of sintered HAp- Al_2O_3 coated ZrO_2 composites.The amounts of major phases present in the respective samples are given in the Table 4.1.

Table .4.1 The amount of major phases present in the different samples.

Composition	Relative Sintered Density (%)	Phases in Sintered HA Sample (vol%)				
		HA	TZP+ αTCP	TZP	CZ	β–TCP
HA	98.0	100	-	-	-	-
HZ10	91.2	61	-	22.68	-	16
HA10	62.32	49	-		6	44
9H1AZ	78.61	63.24	-	23.52	-	13.24
9H2AZ	71.62	28.47	26.15	-	-	42.36
9H3AZ	70.3	58.78	-	24.83	-	16.38
9H5AZ	57.62	34.74	29.74	-	-	35.50

The results show that the degree of reaction of HAp was less in case of HAp-TZP composite. However, there was significant reaction of HAp with Al_2O_3. These adverse reactions increased with the increase in alumina content in the system. This result contradicts the previously found observation of Kong et al [6], who reported that degree of decomposition of HAp with ZrO_2 is more than that with Al_2O_3. For further comparison, we studied different HAp- Al_2O_3 coated ZrO_2. It was inferred that the reaction tendency of HAp with HAp- Al_2O_3 coated ZrO_2 composites was less compared to HAp with HAp- Al_2O_3 composites. The decomposition tendency was found to increase with the increase in Al_2O_3 content in the composites.

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Chapter 5

CONCLUSION

The HAp-Al_2O_3 coated ZrO2 was prepared by chemical precipitation route. The decomposition of the HAp increased with the increase in Al_2O_3 content in the composite matrix. The decomposition of the HAp with the TZP system was found to be less as compared to Al_2O_3 containing systems. 10% TZP containing HAp retained only 16% of β–TCP after sintering, while 10% Al_2O_3 containing HAp ended up with 44% of β–TCP. The amount of β–TCP formed increased with the increase in Al_2O_3 content. This result contradicts the previously conducted studies.

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